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Design and synthesis of mesoporous ZrO₂ thin films using surfactant Pluronic P123 via sol-gel technique

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Mesoporous ZrO₂ thin films were fabricated via sol-gel technique by introducing a surfactant, Pluronic P123. The mesoporous structure was tailored by altering several key processing variables including calcination temperature and heating rate. The samples prepared were characterized systematically with X-ray diffraction and electron microscopy. The pore size of the mesoporous ZrO₂ synthesized was ca. 8 nm and the corresponding thin film thickness was ca. 60 nm. It was found that at a relatively high heating rate, the mesoporous ZrO₂ produced had partially-ordered mesoporous structure and its wall structure was semi-crystalline. A mechanism was proposed for this structure formation.

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Key-words : ZrO₂, Sol-gel, Pluronic P123, Mesoporous, Thin film

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1. Introduction

A new family of mesoporous SiO₂ was pioneered by Waseda University¹⁾ and Mobile Cooperation groups²⁾ in the beginning of 1990s. Ever since, enormous works involving various sol-gel precursors combined with various surfactants have been reported. The fabrication of mesoporous materials composed of crystalline wall structure has attracted significant interest owing to their diverse (e.g. catalytic, optical, electronic and magnetic) properties, which combine the features of a mesoporous material such as high surface area and porosity with the good physical properties of the metal oxide.³⁾

The study on mesoporous materials started from and still mainly focused on the synthesis of SiO₂-based materials.⁴⁾ It can be attributed to the fact that most of the research groups working with mesoporous materials have their origin in the chemistry of zeolites, and thus are much more familiar with the chemistry of the silicates and aluminosilicates than with that of transition metals (TM). The main reason lies probably in the less explored and complex chemistry of TM oxide (TMO) when compared to that of SiO₂.⁵⁾ Thus, TMO based mesoporous materials are generally more difficult to prepare. In contrast to silicon, TMs generally: (1) possess high reactivity toward hydrolysis and condensation; (2) tend to form random and so-called "close" objects instead of fractal objects that can be obtained from SiO₂; (3) possess complex oxidation and coordination states; and (4) transform into oxides which have relatively low thermomechanical stability originated from low temperature crystallization.

Surfactant-templated mesoporous materials of TMO have wide domain of applications, associated to their good semiconductivity, high refractive index,⁶⁾ excellent electronic and magnetic properties over SiO₂.⁴⁾ Among the TMOs, ZrO₂ has attained attention because it substantially exceeds SiO₂ in terms of

mechanical stability and would be ideal mesoporous materials for various applications.³⁾ In particular, high surface area of mesoporous ZrO₂ is a very interesting, in view of sensors, electrochemical devices, optical devices, membrane reactors and microelectronics applications.⁷⁾ For many of these applications, processing the material as a thin coating is important.⁴⁾ In the case of the fabrication of metal-oxide-semiconductor (MOS) capacitor type gas sensor, TMO thin film plays an important role in the detection of different gas species.⁸⁾⁻¹⁰⁾ For instance, ZrO₂ thin film appears to be a suitable candidate as a gate oxide material in the fabrication of Si-based MOS capacitor O₂ sensor at room temperature.¹¹⁾ The number of studies on the use of mesoporous ZrO₂ as a MOS capacitor type gas sensor is, however, limited, but evidently the surface area and the porosity represent a major factor that governs the adsorption rate and the degree of dissociation of gaseous species onto the sensor.^{3),12)} The control of porous structure of ZrO₂ thin film leads to the tailored properties for respective applications. For the application of ZrO₂, the crystallization can enhance the mechanical and chemical stability. In order to obtain crystalline ZrO₂, calcination temperatures higher than 400°C are required when metal alkoxides are used as precursors. However, the mesostructures of ZrO₂ thin films collapse readily upon calcination at temperatures as high as 400°C due to the atomic rearrangement followed by the crystallization. Thus, there are only a few works reported on the synthesis of mesoporous ZrO₂ thin films with semi-crystalline wall structure, where both amorphous and tetragonal ZrO₂ coexist in the framework.^{5),13)}

On the other hand, there are a number of literature reporting on the synthesis of mesoporous ZrO₂ powders.¹³⁾⁻²⁰⁾ The pioneering work by the research group of Sanchez²¹⁾ represents the preparation of oriented mesostructured ZrO₂ based hybrids and mesoporous ZrO₂ films using diblock copolymer of Brij 58 (C₁₆H₃₃EO₁₀) as structuring agent. The mesopore size obtained was ca. 3.5 nm. The oxide presented regularly ordered long-range

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Table 1. Summary of exemplary reports on synthesis of mesoporous ZrO₂ thin films

	Surfactant	Inorganic precursor	Coating method	Mesostructure	Pore size (nm)	Thickness (nm)
Crepaldi, 2001 ²⁰⁾	Brij 58	ZrCl ₄	Dip-coat	2D-hexagonal at 60°C; 2D-centred rectangular at 300°C	≈3.5	≈300
Crepaldi, 2003 ⁵⁾	Pluronic F127; Brij 58	ZrCl ₄	Dip-coat	2D-hexagonal	—	≈300
Fang, 2007 ²¹⁾	KLE	ZrCl ₄	Dip-coat	2D-hexagonal	≈7.1	—
Krylova, 2009 ²²⁾	Pluronic P123	Zr(OC ₃ H ₇) ₄	Dip-coat	Worm-like	—	—
Wang, 2009 ⁷⁾	Pluronic F127	Zr(OC ₃ H ₇) ₄	Spin-coat	2D-cubic treated by supercritical CO ₂	≈8.5	≈130
Miko, 2010 ²³⁾	Brij 700	ZrOCl ₂ ·8H ₂ O	Spin-coat	—	4–8	150

patterns at the calcination temperature as low as 60°C. The pore shapes became eclipse, which is claimed as the characteristic of entangled worm-like channels, by increasing the calcination temperature to 300°C after a two-step process (first drying then treatment at high humidity followed by second drying). Two years later, the same research group⁵⁾ reported on the synthesis of mesoporous ZrO₂ thin films with semicrystalline tetragonal ZrO₂ walls by using triblock copolymer of Pluronic F127 (EO₁₀₆PO₇₀EO₁₀₆) as surfactant. The thermal stability of the mesoporous thin films was enhanced up to 400°C by applying the two-step process. **Table 1** shows the summary of the exemplary works that focus on the synthesis of mesoporous ZrO₂ thin films, which mainly used non-ionic block copolymers as the structure directing agent.

In this work, metal alkoxide precursor and Pluronic surfactant were used to produce mesoporous ZrO₂ thin films. The formed mesoporous ZrO₂ thin films with semi-crystalline wall structure possessed worm-like mesopores with partially ordered porous structure. The maximum pore size of the mesostructure was ca. 8 nm and the thickness of the thin film formed was ca. 60 nm. The other profound finding in this work is the formation of long-range ordered mesoporous structure of ZrO₂ thin films at a relatively high heating rate (5°C/min)^{5),21),22)} during calcination process.

2. Experimental procedure

2.1 Chemicals

Zirconium(IV) butoxide (Zr[O(CH₂)₃CH₃]₄, Sigma-Aldrich), acetylacetone (AcAc, Wako), ethanol (EtOH, Wako), nitric acid (HNO₃, 1 M, Wako) and poly(alkylene oxide) copolymer HO(CH₂CH₂O)₂₀(CH₂CH(CH₃)O)₇₀(CH₂CH₂O)₂₀H (designated EO₂₀PO₇₀EO₂₀; Pluronic P123, Sigma-Aldrich) were used as received. Water was distilled and deionized. The RCA solution for cleaning of the Si substrates was prepared by mixing H₂O, ammonia solution (NH₃, 28 wt %, Wako) and hydrogen peroxide (H₂O₂, 30 wt %, Wako) in the volume ratio of 5:1:1.

2.2 Sample preparation

EtOH was used as a solvent for Zr[O(CH₂)₃CH₃]₄.²³⁾ The hydrolysis of Zr[O(CH₂)₃CH₃]₄ is very fast in the presence of water, resulting in the formation of precipitated hydroxides. Thus, AcAc as a chelating agent was selected for the chemical modification of Zr[O(CH₂)₃CH₃]₄. During the hydrolysis of Zr[O(CH₂)₃CH₃]₄, HNO₃ was added into the EtOH solution to create an acidic condition for the prevention of immediate precipitation of ZrO₂. The molar ratio of Zr[O(CH₂)₃CH₃]₄, EtOH, AcAc, H₂O and HNO₃ used were 1.25, 40, 1, 3.2 and 0.8 respectively. Specifically, Zr[O(CH₂)₃CH₃]₄ and EtOH were mixed and stirred at room temperature. After 30 min, AcAc was added into the solution and the solution was stirred for 30 min followed by the addition of HNO₃ with continuous stirring for

60 min. Meanwhile, Pluronic P123 (1 g) was dissolved in 20 ml EtOH by stirring the solution at room temperature for 30 min until a clear and homogenous solution was obtained. Subsequently, the dissolved Pluronic P123 was added dropwise into 20 ml of the Zr[O(CH₂)₃CH₃]₄-containing solution. The solution was stirred for 130 min. The final solution was used for dip-coating (withdrawing speed: 1.95 mm/s) on one side of Si substrates in a dry atmosphere (<10% R.H.). The dip-coated samples were dried at room temperature for a day. On the other hand, in order to produce ZrO₂ powders, a certain amount of the sol was dried at 60°C for 144 h. Both the thin films and powders produced were calcined at the selected heating temperature and heating rate at the holding time of 4 h.

2.3 Characterization methods

Structural analyses of the films were performed with an X-ray diffractometer (XRD, Rigaku RINT-2000). Both low-angle (1–5)° and wide-angle (10–70)° patterns were obtained. The mesostructure of the prepared materials was observed by a field emission scanning electron microscope (FESEM, S-4800 Hitachi) and a transmission electron microscope (TEM, Hitachi H-800).

3. Results

Figure 1 shows the wide-angle XRD patterns of the prepared ZrO₂ powders before and after calcination. The ZrO₂ sample before calcination showed no diffraction peak, indicating that the sample is amorphous. By calcining the sample at 400°C, the ZrO₂ remained to be amorphous. By increasing the calcination temperature to 450°C, tetragonal ZrO₂ was formed.

Figure 2 shows the low-angle XRD patterns of ZrO₂ thin films calcined at different temperatures and heating rates. There are three dissolved peaks appearing in the range of 1 to 2°. Most of the literature works reported on the formation of two-dimensional

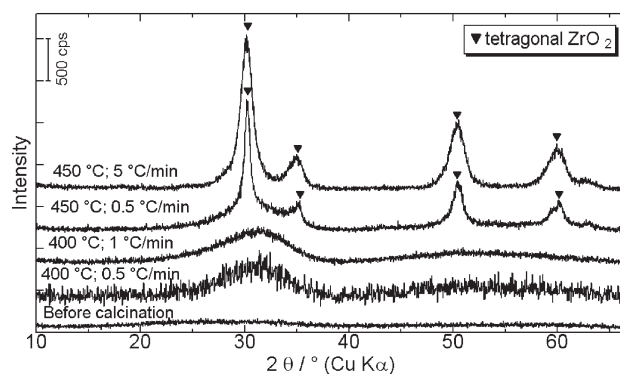


Fig. 1. Wide-angle XRD patterns of the mesoporous ZrO₂ powders before and after calcination. The samples were calcined at 400 or 450°C for 4 h at different heating rates.

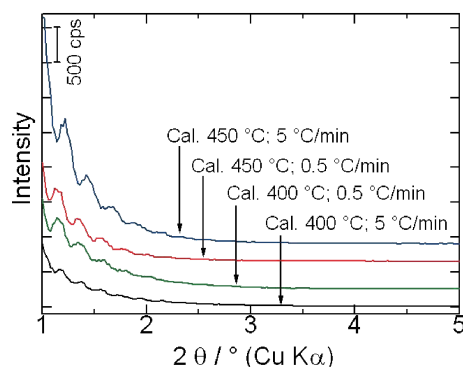


Fig. 2. (Color online) Low-angle XRD patterns of the mesoporous ZrO_2 thin films after calcination. The samples were calcined at 400 or 450°C for 4 h at the heating rate of 0.5 or 5°C/min.

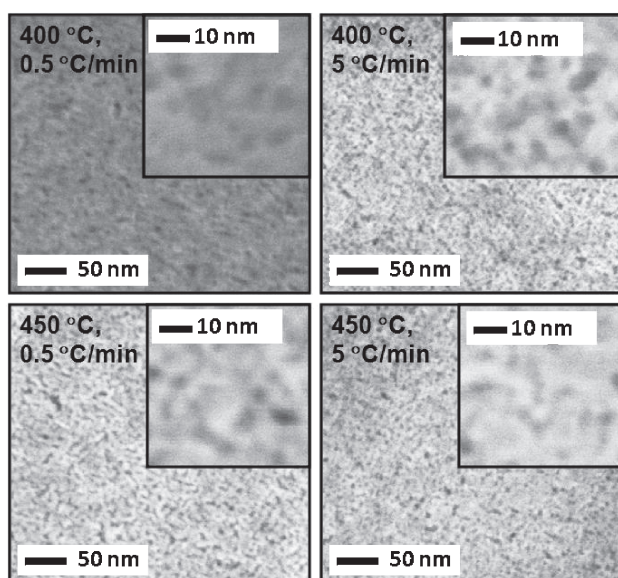


Fig. 3. SEM images of the surface morphology of mesoporous ZrO_2 thin films after calcination. The samples were calcined at 400 or 450°C for 4 h at the heating rate of 0.5 or 5°C/min.

hexagonal or cubic ZrO_2 ordered mesostructures.^{5),7),21),24)} However, the three peaks observed in our samples were not attributed to any of the ordered mesostructures reported so far. Thus, it can be said that disordered mesostructures were formed in the thin films. Nevertheless, periodic nanostructures were assumed to be formed in some part of the disordered mesoporous ZrO_2 thin films, which is revealed in the existence of the three peaks in the low-angle XRD patterns of the samples prepared under different conditions. The ZrO_2 thin film which was calcined at 450°C for 4 h at 5°C/min illustrated relatively stronger peaks compared with the other samples. This implied that the periodic nanostructure in this film sample exists somehow widely and/or more ordered compared with the other samples.

The SEM images of the surface morphology of the ZrO_2 thin films after calcination are shown in Fig. 3. All the samples showed the randomly arranged worm-like mesoporous structure with the pore size is ranging from 3–8 nm. These results confirmed the low-angle XRD results which showed that disordered mesoporous ZrO_2 was mainly formed in the film.

The thickness for the ZrO_2 thin film was measured by using cross-sectional SEM. For the ZrO_2 thin film calcined at 450°C for

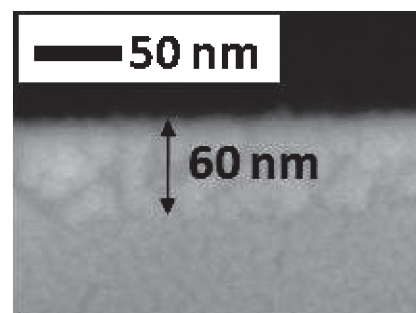


Fig. 4. SEM image of the cross section of mesoporous ZrO_2 thin films after calcination at 450°C for 4 h at the heating rate of 0.5°C/min.

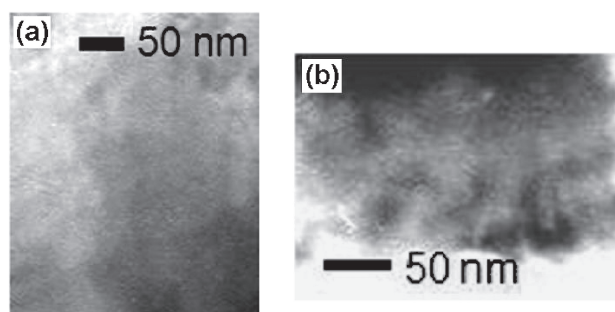


Fig. 5. TEM images of the mesoporous ZrO_2 powders after calcination. The selected samples were calcined at (a) 400°C and (b) 450°C respectively for 4 h at the heating rate of 0.5°C/min.

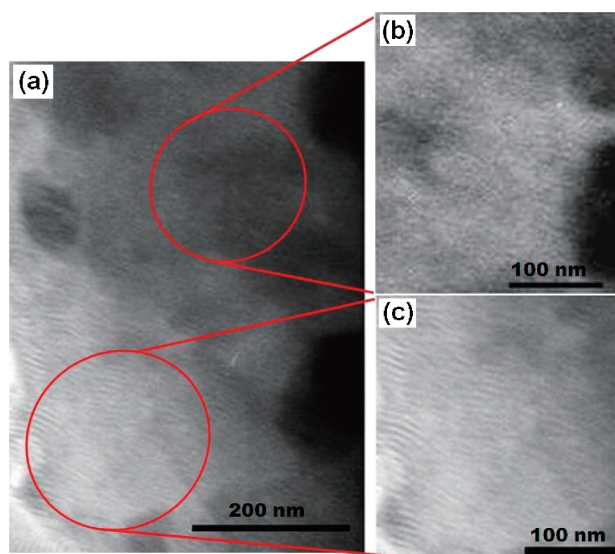


Fig. 6. (Color online) (a) TEM image of mesoporous ZrO_2 powders after calcination at 450°C for 4 h at the heating rate of 5°C/min. (b) and (c) are the magnified images at the circled regions.

4 h at the heating rate of 0.5°C/min, the thickness obtained was 60 nm (Fig. 4). The other films possessed the almost same thickness as this film.

The TEM images of the ZrO_2 samples after calcination are shown in Figs. 5 and 6. For all the calcined ZrO_2 samples, worm-like mesostructures were mainly observed. This result obtained was consistent with the SEM results which showed the surface morphology of worm-like mesostructures. However, as for the ZrO_2 sample which was calcined at 450°C for 4 h at the heating rate of 5°C/min (Fig. 6), the ordered mesoporous structure was

distinguishably observed. The partial-ordered mesopores which were recognized as tube- or lamellar-like mesopores were formed concurrent with the disordered worm-like mesostructure.

4. Discussion

For the sample calcined at 450°C with the heating rate of 5°C/min, the ordered mesoporous structure associated with the worm-like mesopores was obtained [Fig. 6(c)]. This long-range ordered mesostructure reveals that at a high heating rate, the long-range mesostructure was preserved. This is a new finding where most of the works utilize relatively lower heating rate during calcination for template removal to avoid the collapse of the mesostructure. Moreover, the ZrO₂ wall structure formed was semi-crystalline with tetragonal ZrO₂.

Prolonging the holding time during calcination while maintaining the calcination temperature (400°C) and heating rate (0.5°C/min) did not help in obtaining ordered mesoporous structure of ZrO₂; the longer holding time rather caused the gradual collapse of long-range ordered mesoporous structures, and worm-like mesostructures were obtained (data not shown).

Crepaldi et al.⁵⁾ reported that the drying process right after the deposition of the mesoporous ZrO₂ thin films readily results in the formation of condensed inorganic species, by which the worm-like mesostructures are “frozen”. Besides, according to Mondal et al.,²⁵⁾ most of the mesostructured ZrO₂ generally have relatively thin and fragile wall with amorphous structure, and relatively poor thermal stability compared with the other oxide systems. Such mesoporous structure usually collapses at the crystallization temperature of the inorganic framework. However, many applications of mesoporous ZrO₂, such as high-temperature catalytic reactions of fuel cells, require crystallized wall structures because of the high structural strength and electromagnetic properties. Besides, it is famous that tetragonal ZrO₂ is a technologically significant material that finds extensive use as a catalyst or catalyst support, and oxygen sensor. In this work, a partial but long-range ordered mesoporous structure with worm-like mesopores in ZrO₂ thin films which have partial tetragonal crystal structure was successfully produced at 450°C and at the relatively high heating rate of 5°C/min.

Pluronic P123 is completely removed at above 400°C from the as-synthesized Zr composites, thus, the mesoporous ZrO₂ is formed. However, the mesostructures formed are mainly disordered, which are worm-like mesostructures.²⁶⁾ In our case, by increasing the calcination temperature to 450°C, the amorphous ZrO₂ wall becomes semi-crystalline tetragonal ZrO₂ phase due to an increase in the amount of energy provided. In the case of applying relatively high heating rate at 5°C/min during calcination, the long-range ordered mesoporous structure was partly obtained. Here, we suggest two possible reasons why the ordered mesostructure was obtained in the sample: i) Before calcination, the sample (gel film) possessed well-ordered mesostructure, which was confirmed by strong peaks in the XRD pattern (data not shown). Thus, the relatively quick heating at high temperatures (e.g. 450°C) can partially preserve the ordered mesostructure. However, since the calcination at relatively low temperatures (e.g. 400°C) with the high heating rate (5°C/min) collapsed the ordered mesoporous structure, this mechanism mentioned is somehow contradictory. ii) The formation of tetragonal ZrO₂ wall structure causes the rearrangement of the worm-like mesopores. At the relatively high heating rate, some of the disordered mesostructures are partly recombined to form long-range ordered mesoporous structure. By applying the low heating rate of 0.5°C/min during calcination,

which means the longer dwelling time at the increasing high temperature, the size of the tetragonal ZrO₂ formed becomes larger. Robust framework of ZrO₂ and large mechanical energy are needed to stabilize the system. Thus, the rearrangement from worm-like mesopores to the final ordered mesostructures may be suppressed. These two hypotheses are still controversial, and thus further experiments are required.

It is important to state that PEO-based surfactants are known to adopt one- and two-dimensional micelle structures in aqueous solution.²⁷⁾ The pore structures of the ZrO₂ samples prepared with Pluronic P123 basically reflect the two-dimensional motif of the micellar structure, as evidenced by the representative SEM and TEM images.

Zirconium alkoxide is rapidly hydrolyzed and polymerized to form colloids, and the development of the alkoxide-derived colloids occurs via an aggregation-condensation. Thus, when zirconium alkoxide is used as a precursor for the preparation of mesoporous ZrO₂ in the presence of Pluronic P123, partly hydrolyzed zirconium alkoxide will aggregate rapidly before interaction with surfactant molecule and further self-assembly. This is one of the reason proposed in the literature written by Huang et al.²⁸⁾ why arrangement of micelles in a well-defined geometry is difficult for ZrO₂ to the extent that it is for SiO₂. However, the preparation of ordered mesoporous ZrO₂ thin films will open new industries, and hence is highly worth challenging.

5. Conclusion

In the present study, mesoporous ZrO₂ thin films of worm-like and partly ordered mesoporous structure with semi-crystalline ZrO₂ wall were obtained via sol-gel route. The maximum pore size of ZrO₂ thin film was ca. 8 nm while the thickness of the film was ca. 60 nm. The formation mechanism of the ordered mesoporous structure with semi-crystalline ZrO₂ was proposed. The mesoporous structure of the ZrO₂ thin films, especially whether the ordered mesopores are preserved or not, was found to be affected by the heating temperature and rate.

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